

Viscosity of dilute gases and vapors

(fluidity/molal volume/polyatomic molecules)

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ABSTRACT The well-known formula for calculating the viscosity of hard sphere gases, $\eta_o = 2(mkT)^{1/2}/3\pi^{3/2}\sigma^2$, where σ^2 is molecular cross section, is altered to $\eta_o = K(MT)^{1/2}/V_o^{2/3}$, where V_o is the molal volume of a liquid that has expanded sufficiently to permit mean free paths long enough to have significant fractions of the random thermal momenta of molecules in free flight and M is molal mass.

This formulation places upon a single straight line points for all nonpolar molecules, mono- and polyatomic molecules alike, over long ranges of temperature.

Kinetic theory has yielded the equation

$$\eta_o = 2(mkT)^{1/2}/3\pi^{3/2}\sigma^2 \quad [1]$$

for the viscosity of a dilute gas of hard sphere molecules. m is molecular mass, σ is molecular diameter, k is the Boltzmann constant, and T is the thermodynamic temperature. η_o is the vector momentum applied to produce flow; $(mkT)^{1/2}$ represents the randomly oriented thermal momenta that produce viscosity.

Sigma is not a satisfactory parameter because it is calculated either from Eq. 1 or by some method that assumes an expression for pair-potentials, such as the familiar 6-12 potential of Lennard-Jones, not valid for polyatomic molecules (see ref. 1). Accordingly, I substitute for σ^2 values of $V_o^{2/3}$, where V_o is intrinsic molar volume of a liquid obtained from the linear relation between molal volume V and fluidity, ϕ in the equation (2, 3)

$$\phi = B(V - V_o)/V_o \quad [2]$$

Eq. 1 can then be written

$$\eta_o = K(MT)^{1/2}/V_o^{2/3} \quad [3]$$

where M is the molal mass. We (4) applied this to data for propane and CO_2 , with V_o values 61.0 and 28.4 $\text{cm}^3 \text{mol}^{-1}$, respectively, and obtained $K = 1.36 \times 10^{-3}$ for propane and 1.38×10^{-3} for CO_2 .

We found that the linear relation between ϕ and V holds to large pressures and smaller volumes, also to volumes approximately of half of critical volumes, but as critical volumes are approached, the straight line splits into isotherms that bend toward the horizontal and approach constant fluidity at high dilution. Viewed from the standpoint of viscosity, the reciprocal of fluidity, in Fig. 1, for propane, reproduced from refs. 4 and 5, the split occurs at the volume V_t , where η_a is the contribution of crowding to viscosity calculated by Eq. 2. As η_a approaches zero, η_b increases to η_o , beginning at V_t . The shape of η_b is given by the equation

$$\eta_b = \eta_o(1 - V_t/V). \quad [4]$$

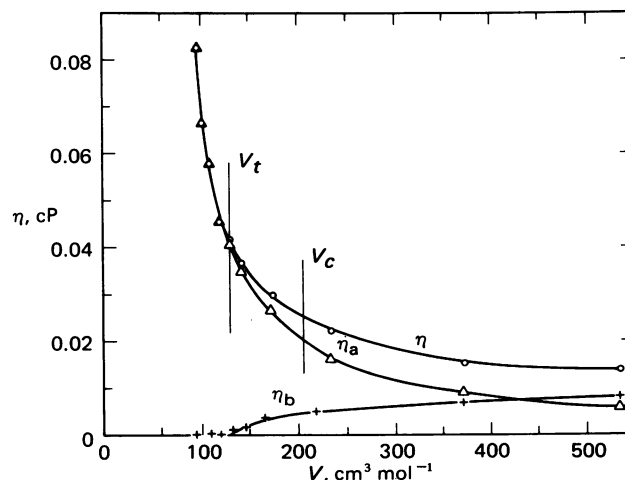


FIG. 1. Relation between the viscosity of propane at 410.9 K and its components η_a and η_b . cP is centipoise; 1 P = 1 $\text{g cm}^{-1} \text{sec}^{-1}$.

In order to obtain precise values of V_t from plots of experimental points of either fluidity or viscosity, there must be an adequate number of points. This is not the case for all of the gases here considered. The available data for neon are plotted as an example in Fig. 2, where there is a gap between 20 and 30 $\text{cm}^3 \text{mol}^{-1}$. How I have handled such cases will be described below.

This paper deals with the nine gases listed in Table 1 and in Fig. 3, where values of viscosity over temperature ranges of from 100° to 200° are plotted against $(MT)^{1/2}$. I invite attention, first, to the straightness of all the lines over their ranges of temperature, as demanded by kinetic theory.

The ratios of V_t/V_o given in Table 1 increase strongly with molecular atomicity and consequent capacity to absorb vector

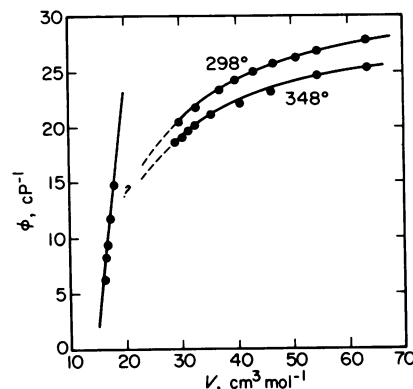


FIG. 2. Fluidity of neon at 298 K and 348 K, showing gap in data between 20 and 30 $\text{cm}^3 \text{mol}^{-1}$.

Table 1. Molal volumes, cm³

Gas	V_o	V_t	$V_t^{2/3}$	V_t/V_o
Ne	14.0	16.6	6.2	1.19
CH ₄	32.0	39.3	11.4	1.23
Ar	24.5	39.5	11.5	1.49
CO ₂	23.4	60.0	15.3	2.11
C ₂ H ₆	44.6	64.0	16.0	1.43
Br ₂	45.8	72.5	17.4	1.58
C ₃ H ₈	61.0	102	21.7	1.67
<i>n</i> -C ₄ H ₁₀	78.5	133	26.0	1.70
CHCl ₃	69.9	170	30.6	2.43

V_o is the intrinsic molal volume at zero fluidity; V_t is the molal volume when the gas is expanded sufficiently to permit linear randomly oriented thermal momenta.

References: summary in ref. 6; ref. 7 and ref. 8.

momentum instead of only distributing it from one molecule to another, as with hard spheres.

In Fig. 4, the viscosities are plotted against $(MT)^{1/2}/V_t^{2/3}$ for gases here considered. Only two values at the extremes are plotted to avoid crowding. In cases where data do not fix values accurately, values of $V_t^{2/3}$ have been adjusted to conform to the single line yielded by cases more clearly indicated. In the cases of bromine and chloroform I simply picked a value of $V_t^{2/3}$ that places all of their points upon the common line. This

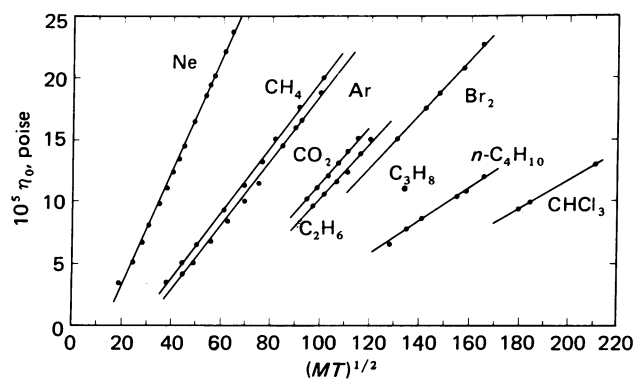


FIG. 3. Linear variations of viscosities of gases and vapors with values of $(MT)^{1/2}$. The units of MT are g °K mol⁻¹.

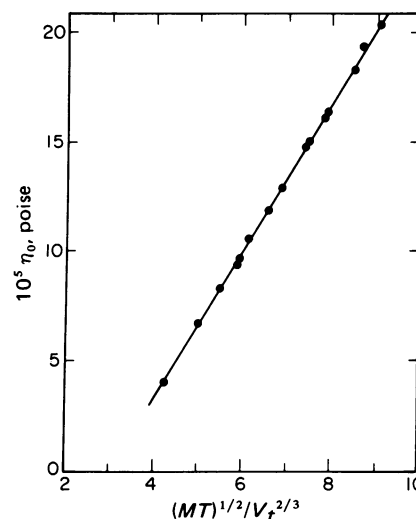


FIG. 4. Viscosities of nine dilute gases and vapors which all fall upon a single line when plotted against $(MT)^{1/2}/V_t^{2/3}$. The units on the abscissa are (g °K mol⁻¹)^{1/2}/(cm³ mol⁻¹)^{2/3}.

procedure will suffice to predict the whole temperature range of viscosity of a gas or vapor from a single measurement.

The equation for the line in Fig. 4 is

$$\eta_o = 3.33[(MT)^{1/2}/V_t^{2/3} - 3].$$

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